Organic Syntheses via Transition-Metal Complexes. 110.[1] A Convenient Regio- and Stereoselective Approach to the Angular Allylation of Bicyclic Cyclopentadienes Generated by the (1-Alkynyl)carbene Complex Route

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Received January 22, 2001

Reaction of the [2-(1-cyclopentenyl)ethynyl]carbene tungsten compound **1a** with secondary allylamines RNH−CH_2CH=CH_2 (R = CH_2CH=CH_2, $CH_2CH_2CH_3$, $PhCH_2$) (**2a**−**c**) and pyridine affords (*C6a*-allyltetrahydropentalen-1-ylidene)amines **3a**−**c** in 72−77% yields. Compounds **3** result from a highly regio- and stereoselective *N*,*C*-allyl rearrangement of 1-(allylamino)cyclopentadiene precursors **7**, which are generated in a kinetically controlled process from compound **1a**. The reaction has been successfully extended to the formation of (*C7a*-allylpentahydro-3a*H*-inden-1-ylidene)amines **8a**−**c** from [2-(1-cyclohexenyl)ethynyl]-carbene tungsten complex **1b** and (*C8a*-allylhexahydro-3a*H*-azulenylidene)amines **12a,b** from [2-(1-cycloheptenyl)ethynyl]carbene tungsten complex **1c**.

Introduction

(1-Alkynyl)carbene complexes $(CO)_5M$=C(OEt)C≡CR (M = W, Cr; R = aryl) have been applied as stoichiometric reagents in a number of high-yielding transformations of potential use in organic synthesis.[2] In a prominent example, cyclopentadienes were obtained in [3+2] fashion by condensation of (1-alkynyl)carbene complexes with enamines.[3] The key step of this reaction was shown to involve formation of amino-1-metalla-1,3,5-hexatrienes, which subsequently underwent a π-cyclization to cyclopentadienes.[4,5] A driving force for the π-cyclization of 1-metalla-1,3,5-hexatrienes is provided by, e.g., amino substituents; especially 6-amino,[3,6,7] but also 2-amino[4] and 4-amino,[4,8] substituents were found to promote this reaction.

Until recently, the substitution pattern of cyclopentadienes generated by π-cyclization of 1-metalla-1,3,5-hexatrienes was severely limited by the few routes to 1-metalla-1,3,5-hexatrienes available. Much effort has been made more recently to extend the scope of such reactions. A new and efficient approach to the formation of 1-metalla-1,3,5-hexatrienes from starting components other than enamines involves the addition of protic nucleophiles NuH [NuH = R(R′CO)CH_2,[9] R_2NH,[8] R_2-PH,[8] RC(=O)OH and ROH,[10,11] RC(=X)SH (X = O, NH, NR),[12] and RSH[13]] to [2-(1-cycloalkenyl)ethynyl]carbene complexes **1a**−**c**.[8,14] This reaction mode provides a highly regioselective entry not only to a broad range of substituted cyclopentadienes not available up to date but also to very thermolabile bicyclic cyclopentadienes, which in our hands now prove to be valuable building blocks for the stereoselective generation of polycyclic ring compounds. The regio- and stereochemistry of the latter reactions is influenced not only by the substitution pattern of the cyclopentadiene ring but also by ring strain effects imposed by the annelated ring. This latter feature is illustrated by the completely different reaction courses observed for cyclopentenyl and cyclohexenyl derivatives **1a** and **1b**, respectively.[10,11]

Results and Discussion

While an addition of alcohols or carboxylic acids to tungsten compounds **1a,b** in each case afforded metal-

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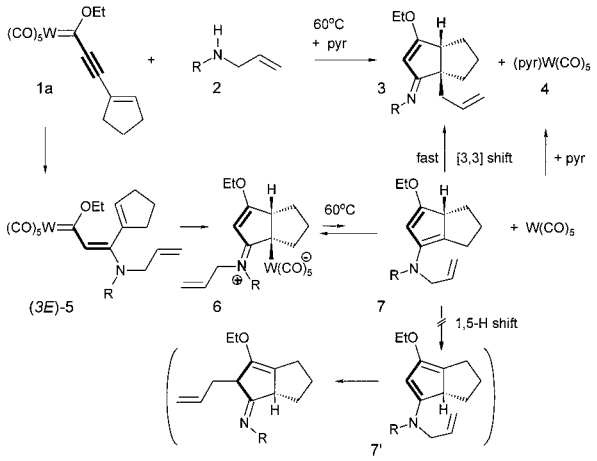
10.1021/om010045o CCC: $20.00
Publication on Web 04/26/2001

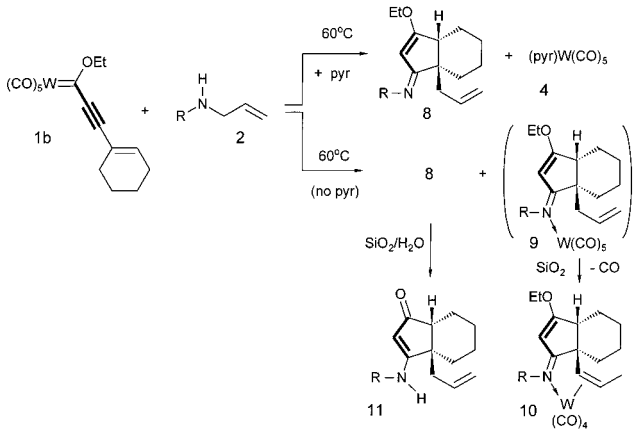
Scheme 1. Generation of Tetrahydropentalenes 7 from [2-(1-Cyclopentenyl)ethynyl]carbene Complex 1a and Their Stereoselective Aza Claisen Rearrangement to Compounds 3



2-6	R	[3] % *[a]*	[5] %	[6] %
a	$H_2C{=}CHCH_2$	77	92*[b]*	86*[b]*
b	$CH_3CH_2CH_2$	72	*[c]*	*[c]*
c	$PhCH_2$	74	*[c]*	*[c]*

[a] Isolated yields by chromatography on silica gel. *[b]* Isolated yields by crystallization. *[c]* Not isolated.

Scheme 2. Angular Allylation Products 8 via Pentahydroindenes Obtained from [2-(1-Cyclohexenyl)ethynyl]carbene Complex 1b



8–11	R	[8] %	[8] %	[10] %	[11] %
a	$CH_2{=}CHCH_2$	85*[a]*	68*[b]*	*[c]*	17*[b]*
b	$CH_3CH_2CH_2$	86*[a]*	65*[b]*	*[c]*	21*[b]*
c	$PhCH_2$	*[c]*	70*[b]*, 43*[d]*	23*[d]*	*[c]*

[a] Total yield of reaction in presence of pyridine. *[b]* Isolated yields by chromatography of the reaction mixture in presence of pyridine. *[c]* Not determined. *[d]* Isolated yield from reaction performed in absence of pyridine.

free cyclopentadienes, addition of secondary amines to [2-(1-cyclopentenyl)ethynyl]carbene complex **1a** gave cyclopentadiene complexes **6**. The latter could be isolated in the form of zwitterionic η^1-tetrahydropentalene iminium pentacarbonyl tungstates (Scheme 1).[8] The reaction course shown in Scheme 1 was exemplified by the generation and isolation of 4-amino-1-metalla-1,3,5-hexatriene complex **5a** from (1-alkynyl)carbene tungsten compound **1a** and diallylamine (**2a**) at 0 °C in 92% yield. Compound **5a** was stable in the solid state, but in C_6D_6 solution at 20 °C, 4 h, it underwent a π-cyclization to give compound **6a** in 86% isolated yield. Even though facile ligand elimination was observed in the mass spectra of compounds **6**, tetrahydropentalenes **7** could not be obtained on a preparative scale, e.g., by ligand elimination with pyridine, due to the high reaction temperature imposed by the stability of compounds **6** on one side and the high thermal sensitivity of the metal-free tetrahydropentalene ligands on the other side.[8] We finally are able to present unambiguous proof that tetrahydropentalenes can indeed be generated by the "(1-alkynyl)carbene route". For the present case, compound **6a** was found to react with pyridine at 60 °C, 2 h, to afford compound **3a** in 77% isolated yield together with (pyridine)$W(CO)_5$ (Scheme 1). It is quite obvious that formation of compound **3a** involves a *N*,*C*-allyl rearrangement (aza Claisen rearrangement) of a tetrahydropentalene precursor, **7a**, which itself is obtained by demetalation of the metal complex with pyridine (Scheme 1). The allyl rearrangement is highly regio- and stereospecific and is faster than the isomerization of compound **7a** to the thermodynamically more stable isomer **7′a** (AM1 calculation: (**7a**) $\Delta H_f = 34.20$ kcal/mol, (**7′a**) 32.87 kcal/mol; experimental proof for a facile 1,5-hydrogen rearrangement of compounds **7** is provided elsewhere[15]). It should be noted that the formation of compound **3a** is kinetically controlled and involves the *N*,*C*-allyl rearrangement of the thermodynamically less stable isomer **7a**, which would not be accessible, e.g., from the corresponding 1,3-diketobicyclo-[3.3.0]octane by conventional routes. The reaction reported above not only is highly stereoselective but also is most conveniently performed in a one-pot procedure directly from the (1-alkynyl)carbene compound **1a**.

Compounds **3**−**6** were identified by their spectroscopic data[8] as well as a crystal structure of compound **6a**.[16] The η^1-coordination of the cyclopentadiene complex **6a** is indicated in the ^{13}C NMR spectrum from the high-field shift of the σ-M−C unit (δ 52.2) and the low-field shift of the C=N unit (δ 192.1). The carbiminium carbonylmetalate structure is further documented by the long distance of the W−C single bond, 2.413(3) Å, and the short distance of the $C{=}N^+$ double bond, 1.335-(4) Å, in line with data found for related compounds.[4a,8]

Our studies on the angular allylation of tetrahydropentalenes by aza Claisen rearrangement could be extended also to the formation of homologous pentahydroindene systems (Scheme 2). Demetalation of the tungsten complex generated by π-cyclization of the initially obtained 4-amino-1-tungsta-1,3,5-hexatriene was achieved at 60 °C. A smooth transformation into a 1:1 mixture of compounds **8** and (pyridine)$W(CO)_5$ was observed in the presence of pyridine. Thermolysis in the absence of pyridine afforded not only appreciable smaller yields of compounds **8** but also chelate complexes **10** in amounts strongly dependent on the reaction conditions. Complexes **10** are assumed to be generated from imino complexes **9** by coordination of the allyl system and a

(15) Wu, H.; Aumann, R. Results to be published.
(16) For details see the Supporting Information.

subsequent metal-induced 1,3-hydrogen shift. While the metal complexes **10** seem to be quite stable on contact with silica gel, chromatography of compounds **8** must be performed fast to avoid a substantial loss of chemical yields from hydrolysis.

The structure of complex **10c** was confirmed by a crystal structure analysis (Figure 1). In line with

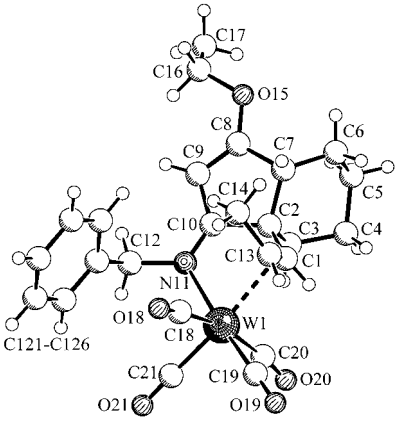


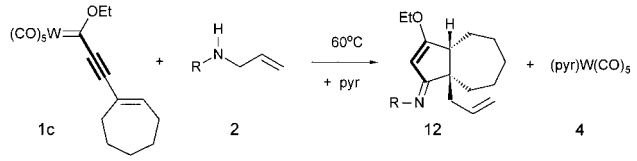
Figure 1. Molecular structure of η^2-(imino,olefin)tetracarbonyltungsten compound **10c**. Selected bond lengths (Å) and bond angles (deg): W1−N11 = 2.253(8), W1−C1 = 2.463(8), W1−C13 = 2.528(8), C1−C13 = 1.375(11), C1−C2 = 1.495(13), C2−C10 = 1.530(10), C2−C7 = 1.554(12), C2−C3 = 1.556(10), C3−C4 = 1.534(11), C4−C5 = 1.553(19), C5−C6 = 1.456(15), C6−C7 = 1.534(11), C7−C8 = 1.508(13), C8−C9 = 1.337(12), C9−C10 = 1.467(14), C10−N11 = 1.275(11), N11−C12 = 1.496(9); N11−W1−C1 = 73.5(3), N11−W1−C13 = 83.7(3), C1−W1−C13 = 32.0(3), C13−C1−C2 = 125.5(8), C13−C1−W1 = 76.6(5), C2−C1−W1 = 106.7(5), C1−C2−C10 = 111.8(7), C1−C2−C7 = 115.4(6), C10−C2−C7 = 103.0(7), C1−C1−C3 = 112.2(8), C10−C2−C3 = 105.1(6), C7−C2−C3 = 108.5(7), C8−C7−C6 = 116.8(8), C8−C7−C2 = 101.4(7), C6−C7−C2 = 117.4(7), O15−C8−C9 = 129.2(9), O15−C8−C7 = 116.4(8), C9−C8−C7 = 114.3(10), C8−C9−C10 = 108.1(8), N11−C10−C9 = 132.1(7), N11−C10−C2 = 120.3(9), C9−C10−C2 = 107.6(8), C10−N11−C12 = 119.1(8), C10−N11−W1 = 118.9(6), C12−N11−W1 = 121.6(6).

expectation, the bond angles N11−W1−C1 = 73.5(3)° and N11−W1−C13 = 83.7(3)° are slightly smaller than 90°. The bond distance of the coordinated double bond is somewhat elongated, C1−C13 = 1.375(11) Å [compared with that of compound **6a**: C14−C15 = 1.282(5) Å] while the bond distance C10−N11 = 1.275(11) Å is slightly shortened [compared with that of compound **6a**: C2−N12 = 1.335 (4) Å].

The angular allylation of bicyclic cyclopentadienes has been extended to ring systems larger than six-membered rings. Examples are provided by the generation of compounds **12a,b** from reaction of [2-(1-cycloheptenyl)ethynyl]carbene tungsten complex **1c** with allylamines **2a,b** (Scheme 3).

Regiochemistry of the *N,C*-Rearrangement. From the studies presented above it is quite obvious that the *N,C*-allyl rearrangement of bicyclic cyclopentadienes affords angular allylation products in high regioselectivity und *cis*-stereoselectivity with respect to the bicyclic ring system (Schemes 2−4).[13] We now present experimental evidence that the *N,C*-rearrangement is highly regioselective concerning the migrating allyl group. Experimental proof is provided by the observation that the *N*-(2-butenyl)benzylamine derivative derived from the reaction of compound **1b** with compound **13** gave a *C*-allylation product **14,** but no isomer **14′**. It thus is obvious that the overall *N,C*-rearrangement involves a [3,3]- but not a [1,3]-process (Scheme 4).

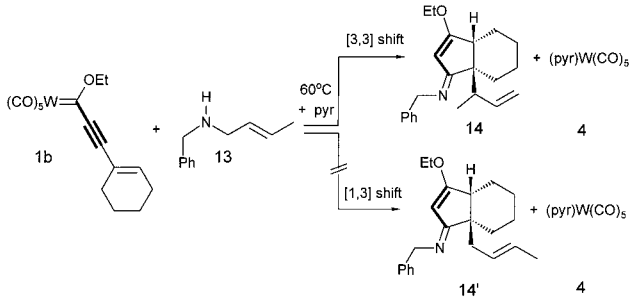
Scheme 3. Angular Allylation Products 12 via Hexahydroazulenes Obtained from [2-(1-Cycloheptenyl)ethynyl]carbene Complex 1c



2, 12	R	[12][a]
a	$H_2C{=}CHCH_2$	72
b	$CH_3CH_2CH_2$	68

[a] Isolated yields by chromatography in %.

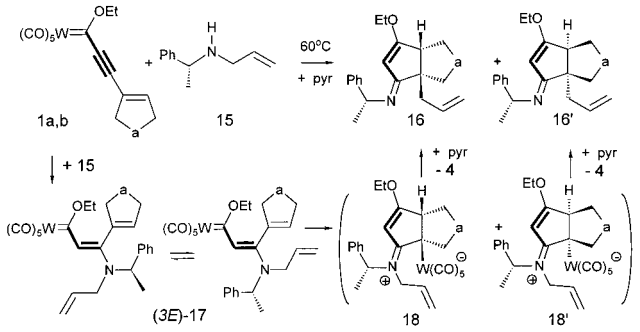
Scheme 4. Regiochemistry of the *N,C*-Rearrangement



Chiral Induction with an Optically Pure Amine. Since it was found that the angular allylation products **3**, **8**, **12**, and **14** were formed from the corresponding cyclopentadiene derivatives with an overall high regio- and stereoselectivity (Schemes 2−4), our investigation was directed toward an enantioselective generation of such compounds by chiral induction of the ring closure of 1-metalla-1,3,5-hexatriene precursors under the influence of an optically active allylamine **15**. Addition of *N*-allyl[(1*R*)-(1-phenylethyl)]amine (**15**) to the (1-alkynyl)carbene complex **1b** afforded the 4-amino-1-tungsta-1,3,5-hexatriene (3*E*)-**17**. The latter compound forms isomers due to hindered rotation of the C−N bond, which can be detected in the ^{1}H NMR spectrum at −40 °C, 600 MHz, by two sets of signals in a ratio of ca. 1:1.[8] Thermolysis of compound (3*E*)-**17** in the presence of pyridine at 60 °C, 2 h, finally gave two diastereoisomers, **16** and **16′**, in a ratio of ca. 3:2 (Scheme 5). An identical ratio of diastereomers was obtained in a one-pot reaction of compound **1b** with compound **15** and pyridine. On the basis of the studies presented above, it is reasonably assumed that the diastereomers **16** and **16′** are derived from the metal complexes **18** and **18′**, which are formed by *anti*-addition of the M═C bond to the terminal C═C bond.[8] The stereocontrol of the π-cyclization is based on the reasonable assumption that an arrangement of the bulky $W(CO)_5$ group *cis* with respect to the angular hydrogen atom of the zwitterionic intermediate should be kinetically strongly favored over formation of a *trans*-arrangement of these groups. It is attributed to steric

effects that the 3:2 stereodiscrimination of compounds **18** and **18′** is much lower than previously observed for the corresponding tetrahydropentalene systems attached to a (2*S*)-(methoxymethyl)pyrrolidine substituent.[8]

Scheme 5. Studies Directed toward a Potential Diastereomeric Discrimination of the Ring Closure of 1-Tungsta-1,3,5-hexatrienes (3*E*)-17 Induced by an Optically Pure Amine, 15



16a/16'a a = CH_2; **16b/16'b** a = CH_2CH_2;

The structural assignment of compounds **16** and **16′** was based on ^{1}H and ^{13}C NMR spectra including COSY HMQC and HMBC experiments. A 3:2 ratio of diastereomers was determined by integration of the signal C*H*═CH_2 of the allyl group [**16a** (**16′a**), δ 5.91 (5.76); **16b** (**16′b**), δ 5.78 (5.94)] and the signal (EtO)C═C*H* of the enol ether unit [**16a** (**16′a**), δ 5.35 (5.36); **16b** (**16′b**), 5.39 (5.36)]. Overlapping signals observed in the ^{13}C spectra were distinguished by their relative intensities observed in the HMQC and HMBC experiments.

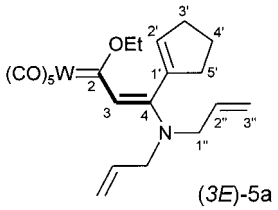
Conclusion

Reaction of [2-(1-cycloalkenyl)ethynyl]carbene tungsten compounds **1a**−**c** with secondary allylamines **2a**−**c** was shown to provide a highly regio- and stereoselective access to angular allylation products of thermodynamically unstable bicyclic 1-aminocyclopentadienes. (*C6a*-allyltetrahydropentalen-1-ylidene)amines **3a**−**c**, (*C7a*-allylpentahydro-3a*H*-inden-1-ylidene)amines **8a**−**c** and (*C8a*-allylhexahydro-3a*H*-azulenylidene)amines **12a,b** could be obtained in a kinetically controlled reaction, due to the fact that the *N*,*C*-migration of the *N*-allyl group of the bicyclic 1-aminocyclopentadienes is much faster than the double bond isomerization of these compounds.

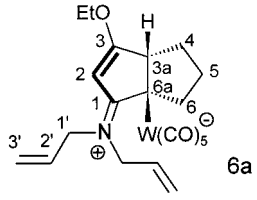
Experimental Section

All operations were carried out under an atmosphere of argon. All solvents were dried and distilled prior to use. All ^{1}H and ^{13}C NMR spectra were routinely recorded on Bruker ARX 300 and AM 360 instruments. ^1J(H,C), ^2J(H,C), and ^3J(H,C) decouplings were recorded on a Varian 400 or 600 instrument if not indicated otherwise. IR spectra were recorded on a Biorad Digilab Division FTS-45 FT-IR spectrophotometer. Elemental analyses were determined on a Perkin-Elmer 240 elemental analyzer. Analytical TLC plates, Merck DC-Alufolien Kiesegel 60_{F240}, were viewed by UV light (254 nm) and stained by iodine. R_f values refer to TLC tests. Chromatographic purifications were performed on Merck Kieselgel 100. Pentacarbonyl(3-cyclopentenyl-1-ethoxy-2-propyn-1-ylidene)-tungsten (**1a**), pentacarbonyl(3-cyclohexenyl-1-ethoxy-2-propyn-1-ylidene)tungsten (**1b**), and pentacarbonyl(3-cycloheptenyl-1-ethoxy-2-propyn-1-ylidene)tungsten (**1c**) were prepared according to ref 8. Secondary *N*-allylalkylamines **2a,b**, **13**, and **15** were generated by reaction of the corresponding primary alkylamines (2.00 mmol) with propenyl bromide and butenyl bromide (1.00 mmol) in diethyl ether (5 mL) at 20 °C, 20 h. A precipitate of primary alkylammonium bromide (identified by a NMR spectrum) was removed by centrifugation. The alkenylamines were isolated from the mother liquor by chromatography on silica gel with *n*-pentane/diethyl ether (5:1) in ca. 50% yields.

1,1,1,1,1-Pentacarbonyl-4-(cyclopent-1-enyl)-2-ethoxy-4-(diallylamino)-1-tungsta-1,3-butadiene [(3*E*)-5a] and (3a*R,6a*R**)-[1-(Diallylazonia)-3-ethoxy-4,5,6,6a-tetrahydro-3a*H*-pentalen-6a-yl]pentacarbonyltungsten (6a).** A solution of diallylamine (**2a**) (49 mg, 0.50 mmol) in 0.5 mL of diethyl ether was added dropwise under stirring to a solution of pentacarbonyl[3-(cyclopent-1-enyl)-1-ethoxyprop-2-yn-1-ylidene]tungsten (**1a**) (237 mg, 0.50 mmol) in 1.5 mL of *n*-pentane in a 2 mL screw-top vessel at 0 °C. After 15 min the mixture was cooled to −20 °C for 2 h to afford yellow crystals of compound **5a**, which were isolated by centrifugation (262 mg, 92%, R_f = 0.7 in *n*-pentane/dichloromethane (2:1)). Compound **5a** is stable in the solid state at −20 °C for several weeks, but undergoes a smooth rearrangement in *n*-pentane/diethyl ether at 20 °C, 4 h, to give compound **6a** (245 mg, 86% isolated yield after 12 h at −40 °C, R_f = 0.6 in *n*-pentane/dichloromethane (2:1)).



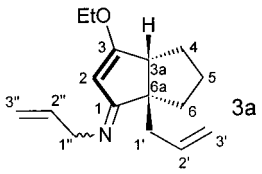
5a. ^{1}H NMR ($CDCl_3$, −20 °C): δ 6.54 (1 H, s, 3-H), 5.81 [2 H, m, 2″-H of N(allyl)$_2$], 5.68 (1 H, m, 2′-H), 5.26 [4 H, m, 3″-H_2 of N(allyl)$_2$], 4.47 (2 H, m, 2-OCH_2), 3.92 [4 H, m, NCH_2 of N(allyl)$_2$], 2.50 (4 H, m) and 2.02 (2 H, m) (3′−5′-H_2), 1.38 (3 H, t, 2-OCH_2CH_3). ^{13}C NMR (C_6D_6): δ 269.4 (C_q, C2), 204.5 and 199.5 [C_q each, *trans*- and *cis*-CO of $W(CO)_5$], 155.7 (C_q, C4), 138.9 (C_q, C1′), 132.4 [2 CH of N(allyl)$_2$], 128.8 (CH, C2′), 119.3 (CH, C3), 118.2 [2 CH_2 of N(allyl)$_2$], 76.2 (OCH_2), 52.9 [2 CH_2 of N(allyl)$_2$], 35.8 and 33.3 (CH_2 each, C3′ and C5′), 22.7 (CH_2, C4′), 15.3 (OCH_2CH_3). IR (diethyl ether), cm^{-1} (%): 2053.7 (5), 1912.3 (100), 1893.6 (70) [ν(C≡O)]. MS (70 eV), *m/e* (^{184}W) (%): 569 (5) [M^+], 429 (40) [M^+ − 5CO]. Anal. Calcd for $C_{21}H_{23}NO_6W$ (569.3): C, 44.31; H, 4.07; N, 2.46. Found: C, 44.56; H, 4.39; N, 2.41.



6a. ^{1}H NMR (C_6D_6): δ 5.59 [2 H, m, 2′-H of N(allyl)$_2$], 4.96 [4 H, m, 3′-H_2 of N(allyl)$_2$], 4.95 (1 H, s, 2-H), 3.85 (1 H, t, 3a-H), 3.67 [4 H, m, NCH_2 of N(allyl)$_2$], 3.50 (2 H, m, diastereotopic OCH_2); 2.35, 2.13, 1.84, 1.49 and 0.98 (1:1:2:1:1 H, m each, 4-, 5-, and 6-H_2), 1.01 (3 H, t, 3-OCH_2CH_3). ^{13}C NMR (C_6D_6): δ 203.1 [C_q, 5 C, $W(CO)_5$], 192.1 and 186.5 (C_q each, C1 and C3), 133.4 and 133.3 [CH each, C2′ of N(allyl)$_2$], 120.4 and 119.4 [CH_2 each, C3′ of N(allyl)$_2$], 95.2 (CH, C2), 68.6 (OCH_2), 67.7 (CH, C3a), 57.8 and 55.3 [NCH_2 each, C1′ of N(allyl)$_2$], 52.2 (C_q, C6a); 40.0 (CH_2, C6), 33.0 (CH_2, C4),

32.1 (CH_2, C5), 14.9 (OCH_2CH_3). IR (diethyl ether), cm^{-1} (%): 2053.9 (5), 1980.3 (20), 1913.3 (100) [ν(C≡O)]. MS (70 eV), *m/e* (^{184}W) (%): 569 (10) [M^+], 513 (10) [$M^+ - 2CO$], 485 (25) [$M^+ - 3CO$], 429 (20) [$M^+ - 5CO$], 245 (90). Anal. Calcd for $C_{21}H_{23}NO_6W$ (569.3): C, 44.31; H, 4.07; N, 2.46. Found: C, 44.51; H, 4.08; N, 2.44. X-ray crystal structure analysis of compound **6a** (code 1395.AUM): formula $C_{21}H_{23}NO_6W$, M = 569.25, yellow crystal, 0.35 × 0.35 × 0.20 mm, a = 10.222(1) Å, b = 18.073(1) Å, c = 12.096(1) Å, β = 101.20(1)°, V = 2192.1(3) Å^3, ρ_{calcd} = 1.725 g cm^{-3}, μ = 53.05 cm^{-1}, absorption correction via SORTAV (0.258 ≤ T ≤ 0.417), Z = 4, monoclinic, space group $P2_1/c$ (no. 14), λ = 0.710 73 Å, T = 198 K, ω and φ scans, 17 940 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin θ)/λ] = 0.65 Å^{-1}, 5010 independent (R_{int} = 0.037) and 4434 observed reflections [$I \geq 2\sigma(I)$], 264 refined parameters, R1 = 0.023, wR2 = 0.054, maximum residual electron density 1.02 (−1.36) e Å^{-3} close to W, hydrogens calculated and refined as riding atoms.[17]

(3a*R,6a*R**)-(6a-Allyl-3-ethoxy-4,5,6,6a-tetrahydro-3a*H*-pentalen-1-ylidene)allylamine (3a).** A mixture of [1-(diallylazonia)-3-ethoxy-4,5,6,6a-tetrahydro-3a*H*-pentalen-6a-y1]-pentacarbonyltungsten (**6a**) (170 mg, 0.30 mmol) and pyridine (24 mg, 0.30 mmol) in 2 mL of benzene was heated to 60 °C, 2 h, and separated by chromatography on silica gel (2 × 10 cm) with *n*-pentane/dichloromethane (1:1) to give yellow pentacarbonyl(pyridine)tungsten. Subsequent elution with diethyl ether/ethyl acetate (1:1) affords compound **3a** (56 mg, 77%, R_f = 0.3 in diethyl ether/ethyl acetate (1:1), colorless oil). It should be noted that chromatography must be completed with 30 min to avoid substantial hydrolysis of this compound. More polar eluents, such as diethyl ether/ethanol (2:1), are recommended as eluant from a longer column of silica gel. Compound **3a** could be obtained also in a one-pot procedure by dropwise addition of diallylamine (**2a**) (49 mg, 0.50 mmol) in 1 mL of benzene to a solution of pentacarbonyl[3-(cyclopent-1-enyl)-1-ethoxyprop-2-yn-1-ylidene]tungsten (**1a**) (237 mg, 0.50 mmol) and pyridine (40 mg, 0.50 mmol) in 1 mL of benzene with stirring in a 2 mL screw-top vessel at 0 °C and subsequent heating of the mixture to 60 °C, 2 h.



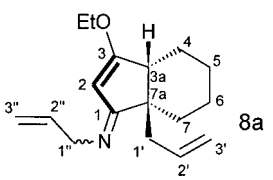
3a. ^{1}H NMR (C_6D_6): δ 6.16 (1 H, m, 2″-H), 5.85 (1 H, m, 2′-H), 5.38 and 5.13 (1 H each, m each, 3″-H_2, ^3J = 17.2 and 11.4 Hz), 5.25 (1 H, s, 2-H), 5.06 and 4.98 (1 H each, m each, 3′-H_2, ^3J = 18.1 and 9.8 Hz), 4.13 (2 H, d, NCH_2), 3.38 (2 H, m, diastereotopic OCH_2), 2.83 and 2.29 (1 H each, dd each, 1′-H_2, J = 8.2 and 13.5 Hz), 2.80 (1 H, m, 3a-H), 2.35 and 1.52 (1 H, m each, 6-H_2), 1.80 and 1.49 (1 H, m each, 4-H_2), 1.44 (2 H, m, 5-H_2), 0.96 (3 H, t, 3-OCH_2CH_3). ^{13}C NMR (C_6D_6): δ 179.7 and 177.3 (C_q each, C1 and C3), 137.9 (CH, C2″), 135.9 (CH, C2′), 117.1 (CH_2, C3′), 114.2 (CH_2, C3″), 95.5 (CH, C2), 66.3 (OCH_2), 57.5 (C_q, C6a), 55.2 (NCH_2), 50.9 (CH, C3a), 43.1 (CH_2, C1′), 38.4 (CH_2, C6), 29.5 (CH_2, C4), 24.8 (CH_2, C5), 14.1 (OCH_2CH_3). IR (diethyl ether), cm^{-1} (%): 1605.1 (50) [ν(C=N)]. MS (70 eV), *m/e* (%): 245 (17) [M^+], 216 (100) [$M^+ - Et$]. HSMS Calcd for $C_{16}H_{23}NO$: 245.17742. Found: 245.17796.

(17) Data sets were collected with a Nonius KappaCCD diffractometer, equipped with a rotating anode generator, Nonius FR591. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN (Otwinowski, A.; Minor, W. *Methods Enzymol.* **1997**, *276*, 307−326), absorption correction SORTAV (Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33−37. Blessing, R. H. *J. Appl. Crystallogr.* **1997**, *30*, 421−426), structure solution SHELXS-97 (Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467−473), structure refinement SHELXL-97 (G. M. Sheldrick, Universität Göttingen, 1997), graphics SCHAKAL (E. Keller, Universität Freiburg, 1997).

(3a*R,6a*R**)-(6a-Allyl-3-ethoxy-4,5,6,6a-tetrahydro-3a*H*-pentalen-1-ylidene)propylamine (3b).** *N*-Allylpropylamine (**2b**) (50 mg, 0.50 mmol) was reacted with pentacarbonyl[3-(cyclopent-1-enyl)-1-ethoxyprop-2-yn-1-ylidene]tungsten (**1a**) (237 mg, 0.50 mmol) and pyridine (40 mg, 0.50 mmol) as described above to give compound **3b** (89 mg, 72%, R_f = 0.3 in diethyl ether/ethyl acetate (1:1), colorless oil). ^{1}H NMR (C_6D_6): δ 5.86 (1 H, m, 2′-H), 5.37 (1 H, s, 2-H), 5.07 and 4.99 (1 H each, m each, 3′-H_2, ^3J = 17.2 and 10.3 Hz), 3.46 (2 H, t, NCH_2), 3.41 (2 H, m, diastereotopic OCH_2), 2.85 and 2.35 (1 H each, dd each, 1′-H_2, J = 7.8 and 13.3 Hz), 2.81 (1 H, m, 3a-H), 2.32 and 1.55 (1 H each, m each, 6-H_2), 1.80 and 1.50 (1 H each, m each, 4-H_2), 1.46 (2 H, m, 6-H_2), 1.85 (2 H, m, 2″-H_2), 1.08 (3 H, t, 3″-H_3), 0.98 (3 H, t, 3-OCH_2CH_3). ^{13}C NMR (C_6D_6): δ 178.8 and 177.2 (C_q each, C1 and C3), 135.1 (CH, C2′), 115.9 (CH_2, C3′), 94.4 (CH, C2), 65.2 (OCH_2), 56.4 (C_q, C6a), 53.7 (NCH_2), 49.8 (CH, C3a), 42.2 (CH_2, C1′), 37.4 (CH_2, C6), 28.6 (CH_2, C4), 23.8 (CH_2, C5), 24.0 (CH_2, C2″), 13.5 (OCH_2CH_3), 11.4 (CH_3, C3″). IR (diethyl ether), cm^{-1} (%): 1604.2 (50) [ν(C=N)]. MS (70 eV), *m/e* (%): 247 (30) [M^+], 219 (100) [$M^+ - C_2H_4$], 191 (90) [$M^+ - C_3H_8N$].

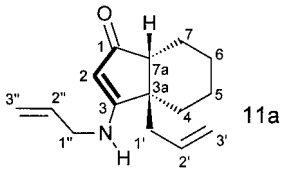
(3a*R,6a*R**)-(6a-Allyl-3-ethoxy-4,5,6,6a-tetrahydro-3a*H*-pentalen-1-ylidene)benzylamine (3c).** *N*-Allylbenzylamine (**2c**) (74 mg, 0.50 mmol) was reacted with pentacarbonyl[3-(cyclopent-1-enyl)-1-ethoxyprop-2-yn-1-ylidene]tungsten (**1a**) (237 mg, 0.50 mmol) and pyridine (40 mg, 0.50 mmol) in 2 mL of benzene as described above to give compound **3c** (109 mg, 74%, R_f = 0.3 in diethyl ether/ethyl acetate (1:1), colorless oil). ^{1}H NMR (C_6D_6): δ 7.55, 7.27 and 7.13 (2:2:1, m each, *o*-, *m*-, and *p*-H of C_6H_5), 5.87 (1 H, m, 2′-H), 5.37 (1 H, s, 2-H), 5.05 and 4.98 (1 H each, m each, 3′-H_2, ^3J = 17.2 and 10.4 Hz), 4.68 (2 H, s, NCH_2), 3.40 (2 H, m, diastereotopic OCH_2), 2.84 and 2.34 (1 H each, dd each, 1′-H_2, J = 8.2 and 13.7 Hz), 2.83 (1 H, m, 3a-H), 2.34 and 1.56 (1 H each, m each, 6-H_2), 1.82 and 1.50 (2.35 and 1.52) (1 H each, m each, 4-H_2), 1.46 (2 H, m, 5-H_2), 0.98 (3 H, t, 3-OCH_2CH_3). ^{13}C NMR (C_6D_6): δ 179.8 and 177.2 (C_q each, C1 and C3), 142.3 (C_q, *ipso*-C of C_6H_5), 135.1 (CH, C2′), 128.5, 127.9, and 126.5 (CH each, 2:2:1, *o*-, *m*-, and *p*-C of C_6H_5), 116.0 (CH_2, C3′), 94.4 (CH, C2), 65.2 (OCH_2), 56.4 (C_q, C6a), 53.7 (NCH_2), 49.8 (CH, C3a), 42.2 (CH_2, C1′); 37.4 (CH_2, C6), 28.5 (CH_2, C4), 23.8 (CH, C5), 13.2 (OCH_2CH_3). IR (diethyl ether), cm^{-1} (%): 1604.0 (50) [ν(C=N)]. MS (70 eV), *m/e* (%): 295 (40) [M^+], 266 (20) [$M^+ - C_2H_5$], 204 (25) [$M^+ - PhCH_2$].

(3a*R,7a*R**)-(7a-Allyl-3-ethoxy-4,5,6,7,7a-pentahydro-3a*H*-inden-1-ylidene)allylamine (8a) and (3a*R**,7a*R**)-8a-Allyl-3-(allylamino)-3a,4,5,6,7-pentahydro-7a*H*-inden-1-one (11a).** Diallylamine (**2a**) (49 mg, 0.50 mmol) was reacted with pentacarbonyl[3-(cyclohex-1-enyl)-1-ethoxyprop-2-yn-1-ylidene]tungsten (**1b**) (243 mg, 0.50 mmol) and pyridine (40 mg, 0.50 mmol) in 2 mL of benzene as described above to give compound **8a** (88 mg, 68%, R_f = 0.3 in diethyl ether/ethyl acetate (1:1), colorless oil). Subsequent elution with diethyl ether/ethanol (1:1) affords compound **11a** (20 mg, 17%, R_f = 0.5 in diethyl ether/ethanol (1:1), colorless oil). The separation on silica gel has to be performed fast, since hydrolysis of compound **8a** to give compound **11a** is complete within 30 min.



8a. ^{1}H NMR (C_6D_6): δ 6.17 (1 H, m, 2″-H), 5.89 (1 H, m, 2′-H), 5.41 and 5.14 (1 H each, m each, 3″-H_2, ^3J = 17.2 and 10.2 Hz), 5.29 (1 H, s, 2-H), 5.05 and 5.01 (1 H each, m each, 3′-H_2, ^3J = 15.8 and 10.1 Hz), 4.17 (2 H, d, NCH_2), 3.45 (2 H, m, diastereotopic OCH_2), 2.70 and 2.31 (1 H each, dd each, 1′-H_2, J = 8.5 and 13.3 Hz), 2.65 (1 H, m, 3a-H), 2.01 and 1.58

(1 H each, m each, 7-H_2), 1.72 and 1.55 (1H each, m each, 4-H_2), 1.37 and 1.29 (2 H each, m each, 5- and 6-H_2), 0.98 (3 H, t, 3-OCH_2CH_3). ^{13}C NMR (C_6D_6): δ 180.9 and 179.5 (C_q each, C1 and C3), 137.6 (CH, C2″), 135.6 (CH, C2′), 117.3 (CH_2, C3′), 114.5 (CH_2, C3″), 94.3 (CH, C2), 66.4 (OCH_2), 54.8 (NCH_2), 48.3 (C_q, C7a), 45.3 (CH, C3a), 43.7 (CH_2, C1′); 31.6 (CH_2, C7), 22.6 (CH_2, C4), 19.1 (2 CH_2, C5 and C6), 14.1 (OCH_2CH_3). IR (diethyl ether), cm^{-1} (%): 1604.5 (40) [ν(C═N)]. MS (70 eV), *m*/*e* (%): 259 (20) [M^+], 230 (100) [M^+ − Et]. HSMS Calcd for $C_{17}H_{25}NO$: 259.19360. Found: 259.19285.



11a.

11a. ^{1}H NMR (C_6D_6): δ 7.88 (1 H, br, NH), 5.71 (2 H, m, 2′- and 2″-H), 5.11 (1 H, s, 2-H), 5.07 (4 H, m, 3′- and 3″-H_2), 3.62 (2 H, m, NCH_2), 2.43 (1 H, m, 3a-H), 2.66 and 2.35 (1 H each, dd each, 1′-H_2, J = 8.7 and 14.1 Hz), 2.15, 1.78, and 1.42 (1:2:5 H, m each, 4-, 5-, 6-, and 7-H_2). ^{13}C NMR (C_6D_6): δ 204.2 (C_q, C1), 181.6 (C_q each, C3), 134.6 (CH, C2′), 133.9 (CH, C2″), 118.1 (CH_2, C3′), 116.3 (CH_2, C3″), 98.4 (CH, C2), 48.9 (C7a), 46.8 (C_q, C3a), 47.4 (NCH_2), 41.7 (CH_2, C1′), 32.0 (CH_2, C7), 21.7 (CH_2, C4), 19.4 and 18.9 (CH_2 each, C5 and C6). IR (diethyl ether), cm^{-1} (%): 3276.5 (30) [ν(N—H)], 1651.3 (20) and 1569.3 (40) [ν(C═O)]. MS (70 eV), *m*/*e* (%): 231 (80) [M^+], 190 (90) [M^+ − 41], 160 (100) [190 − 30].

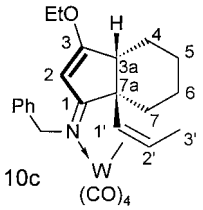
(3a*R,7a*R**)-(7a-Allyl-3-ethoxy-4,5,6,7,7a-pentahydro-3a*H*-inden-1-ylidene)propylamine (8b) and (3a*R**,7a*R**)-8a-Allyl-3-propylamino-3a,4,5,6,7-pentahydro-7a*H*-inden-1-one (11b).** *N*-Allylpropylamine (**2b**) (50 mg, 0.50 mmol) was reacted with pentacarbonyl[3-(cyclohex-1-enyl)-1-ethoxyprop-2-yn-1-ylidene]tungsten (**1b**) (243 mg, 0.50 mmol) and pyridine (40 mg, 0.50 mmol) in 2 mL of benzene as described above to give compound **8b**, if the chromatography is performed fast (85 mg, 65%, R_f = 0.3 in diethyl ether/ethyl acetate (1:1), colorless oil). Subsequent elution with diethyl ether/ethanol (1:1) affords compound **11b** (24 mg, 21%, R_f = 0.5 in diethyl ether/ethanol (1:1), colorless oil). Compound **8b** is completely transformed into compound **11b** on contact with silca gel within 30 min.

8b. ^{1}H NMR (C_6D_6): δ 5.87 (1 H, m, 2′-H), 5.56 (1 H, s, 2-H), 5.08 and 5.02 (1 H each, m each, 3′-H_2, ^3J = 17.2 and 9.9 Hz), 3.54 (2 H, t, NCH_2), 3.57 (2 H, m, diastereotopic OCH_2), 2.82 and 2.35 (1 H each, dd each, 1′-H_2, J = 8.4 and 13.6 Hz), 2.68 (1 H, m, 3a-H), 2.35, 1.68, 1.52, and 1.34 (1:2:1:4 H, m each, 4-, 5-, 6-, and 7-H_2), 1.87 (2 H, m, 2″-H_2), 1.10 (3 H, t, 3″-H_3), 1.01 (3 H, t, 3-OCH_2CH_3). ^{13}C NMR (C_6D_6): δ 179.2 and 177.6 (C_q each, C1 and C3), 135.4 (CH, C2′), 117.4 (CH_2, C3′), 94.7 (CH, C2), 66.8 (OCH_2), 53.8 (NCH_2), 48.3 (C_q, C7a), 43.5 (CH, C3a), 41.9 (CH_2, C1′), 31.7, 22.5, 19.3, and 19.0 (CH_2 each, C4−C7), 24.7 (CH_2, C2″), 14.1 (OCH_2CH_3), 12.3 (CH_3, C3″). IR (diethyl ether), cm^{-1} (%): 1604.9 (50) [ν(C═N)]. MS (70 eV), *m*/*e* (%): 261 (30) [M^+], 232 (90) [M^+ − C_2H_5], 204 (25) [M^+ − C_3H_7N], 192 (100) [M^+ − C_5H_9].

11b. ^{1}H NMR (C_6D_6): δ 7.62 (1 H, br, NH), 5.76 (1 H, m, 2′-H), 5.12 (1 H, s, 2-H), 5.03 (2 H, m, 3′-H_2), 2.95 (2 H, m, NCH_2), 2.45 (1 H, m, 3a-H), 2.70 and 2.35 (1 H each, dd each, 1′-H_2), 2.21, 1.80, and 1.46 (1:2:5 H, m each, 4-, 5-, 6-, and 7-H_2), 1.52 (2 H, m, 2″-H_2), 0.81 (3 H, t, 3″-H_3). ^{13}C NMR (C_6D_6): δ 203.8 (C_q, C1), 181.4 (C_q each, C3), 134.6 (CH, C2′), 118.1 (CH_2, C3′), 97.6 (CH, C2), 48.9 (C7a), 46.9 (C_q, C3a), 46.7 (NCH_2), 41.8 (CH_2, C1′), 32.1, 21.7, 19.5, and 19.0 (CH_2 each, C4−C7), 22.1 (CH_2, C2″), 11.7 (CH_3, C3″). IR (diethyl ether), cm^{-1} (%): 3276.3 (30) [ν(NH)], 1652.2 (20) and 1569.3 (40) [ν(C═O)]. MS (70 eV), *m*/*e* (%): 233 (100) [M^+], 204 (80) [M^+ − C_3H_7N], 192 (100) [M^+ − C_3H_5].

(3a*R,7a*R**)-(7a-Allyl-3-ethoxy-4,5,6,7,7a-pentahydro-3a-inden-1-ylidene)benzylamine (8c).** *N*-Allylbenzylamine (**2c**) (74 mg, 0.50 mmol) was reacted with pentacarbonyl[3-(cyclohex-1-enyl)-1-ethoxyprop-2-yn-1-ylidene]tungsten (**1b**) (243 mg, 0.50 mmol) and pyridine (40 mg, 0.50 mmol) in 2 mL of benzene as described above to give compound **8c** by fast chromatography on silica gel (108 mg, 70%, R_f = 0.3 in diethyl ether/ethyl acetate (1:1), colorless oil). ^{1}H NMR (C_6D_6): δ 7.56, 7.27, and 7.14 (2:2:1, m each, *o*-, *m*-, and *p*-H of C_6H_5), 5.91 (1 H, m, 2′-H), 5.36 (1 H, s, 2-H), 5.04 and 4.99 (1 H each, m each, 3′-H_2, ^3J = 17.1 and 10.3 Hz), 4.70 (2 H, s, NCH_2), 3.44 (2 H, m, diastereotopic OCH_2), 2.72 and 2.37 (1 H each, dd each, 1′-H_2, J = 8.5 and 13.3 Hz), 2.70 (1 H, m, 3a-H), 2.03 and 1.62 (1 H each, m each, 7-H_2), 1.72 and 1.58 (1H each, m each, 4-H_2), 1.59 and 1.33 (2 H each, m each, 5- and 6-H_2), 0.99 (3 H, t, 3-OCH_2CH_3). ^{13}C NMR (C_6D_6): δ 180.6 and 178.9 (C_q each, C1 and C3), 142.3 (C_q, *ipso*-C of C_6H_5), 135.8 (CH, C2′), 128.5, 127.7, and 126.6 (CH each, 2:2:1, *o*-, *m*-, and *p*-C of C_6H_5), 117.2 (CH_2, C3′), 94.3 (CH, C2), 66.3 (OCH_2), 56.2 (NCH_2), 48.4 (C_q, C7a), 45.2 (CH, C3a), 43.8 (CH_2, C1′), 31.7 (CH_2, C7), 22.6 (CH_2, C4), 19.3 (2 CH_2, C5 and C6), 14.1 (OCH_2CH_3). IR (diethyl ether), cm^{-1} (%): 1604.2 (40) [ν(C═N)]. MS (70 eV), *m*/*e* (%): 309 (30) [M^+], 280 (25) [M^+ − C_2H_5], 267 (25) [M^+ − C_3H_6], 218 (30) [M^+ − $PhCH_2$].

(3a*R,7a*R**)-Tetracarbonyl[(3-ethoxy-7a-μ^2-prop-1′-enyl-4,5,6,7,7a-pentahydro-3a*H*-inden-1-ylidene)benzylamine-*N*]tungsten (10c) and (3a*R**,7a*R**)-(7a-Allyl-3-ethoxy-4,5,6,7,7a-pentahydro-3a-inden-1-ylidene)benzylamine (8c).** *N*-Allylbenzylamine (**2c**) (74 mg, 0.50 mmol) was reacted with pentacarbonyl[3-(cyclohex-1-enyl)-1-ethoxyprop-2-yn-1-ylidene]tungsten (**1b**) (243 mg, 0.50 mmol) (in absence of pyridine) in dry diethyl ether at 60 °C, 2 h. The residue thus obtained was separated by fast chromatography on silica gel with *n*-pentane/dichloromethane (2:1) to give compound **10c** (69 mg, 23%, R_f = 0.5 in *n*-pentane/dichloromethane (2:1), yellow crystals from *n*-pentane/diethyl ether (3:1), mp 142 °C) and a more polar colorless fraction containing compound **8c** (71 mg, 46%) (for spectroscopic data v.s.).

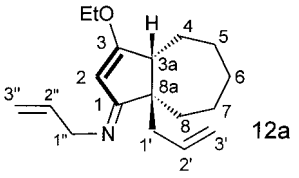


10c

10c. ^{1}H NMR (C_6D_6): δ 7.22−7.08 (5 H, m, *o*-, *m*-, and *p*-H of C_6H_5), 4.70 (1 H, s, 2-H), 4.66 (1 H, d, 1′-H, ^3J = 9.8 Hz), 4.47 and 4.10 (1 H each, d each, NCH_2, ^2J = 14.1 Hz each), 3.99 (1 H, m, 2′-H, ^3J = 9.8 and 6.8 Hz), 3.14 and 3.08 (1 H each, m each, diastereotopic OCH_2), 2.79 (1 H, m, 3a-H), 2.09 and 1.68 (1 H each, m each, 7-H_2), 1.76 and 1.51 (1H each, m each, 4-H_2), 1.45 and 1.32 (2 H each, m each, 5- and 6-H_2), 1.88 (3 H, d, 3′-H_3), 0.86 (3 H, t, 3-OCH_2CH_3). ^{13}C NMR (C_6D_6): δ 191.7 and 182.5 (C_q each, C1 and C3), 137.5 (C_q, *ipso*-C of C_6H_5), 127.9, 126.9, and 126.6 (CH each, 2:2:1, *o*-, *m*-, and *p*-C of C_6H_5), 91.9 (CH, C2), 86.6 and 86.5 (CH each, C1′ and C2′), 66.0 (OCH_2), 62.1 (NCH_2), 53.8 (C_q, C7a), 44.3 (CH, C3a), 32.3 (CH_2, C7), 21.0 (CH_2, C4), 20.7 and 20.0 (CH_2 each, C5 and C6), 15.5 (OCH_2CH_3), 12.8 (CH_3, C3′). IR (diethyl ether), cm^{-1} (%): 2015.5 (20), 1915.0 (30), 1899.2 (100), and 1866.5 (60) [ν(C≡O)]. MS (70 eV), *m*/*e* (^{184}W) (%): 605 (5) [M^+], 493 (30) [M^+ − 4CO], 91 (100). Anal. Calcd for $C_{25}H_{27}NO_5W$ (605.3): C, 49.60; H, 4.50; N, 2.31. Found: C, 49.44; H, 4.25; N, 2.07. X-ray crystal structure analysis of compound **10c** (code 1439.AUM): formula $C_{25}H_{27}NO_5W$, M = 605.33, yellow crystal, 0.30 × 0.20 × 0.10 mm, a = 12.317(1) Å, b = 14.022(1) Å, c = 15.903(1) Å, α = 87.67(1)°, β = 71.29(1)°, γ = 67.04(1)°, V = 2384.1(3) Å^3, ρ_{calcd} = 1.686 g cm^{-3}, μ = 48.80 cm^{-1}, absorption

correction via SORTAV ($0.322 \le T \le 0.641$), $Z = 4$, triclinic, space group $P1$ (no. 2), $\lambda = 0.710\ 73$ Å, $T = 198$ K, ω and φ scans, 23 942 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin θ)/λ] = 0.65 Å^{-1}, 10 759 independent ($R_{int} = 0.048$) and 7783 observed reflections [$I \ge 2\sigma(I)$], 622 refined parameters, R1 = 0.049, wR2 = 0.102, maximum residual electron density 1.73 (−4.07) e Å^{-3} close to W, two almost identical independent molecules in the asymmetric unit, OEt groups heavily disordered and refined with split positions, hydrogens calculated and refined as riding atoms.[17]

(3a*R,8a*R**)-(8a-Allyl-3-ethoxy-4,5,6,7,8,8a-hexahydro-3a*H*-azulen-1-ylidene)allylamine (12a).** Diallylamine (**2a**) (49 mg, 0.50 mmol) was reacted with pentacarbonyl[3-(cyclohept-1-enyl)-1-ethoxyprop-2-yn-1-ylidene]tungsten (**1c**) (250 mg, 0.50 mmol) and pyridine (40 mg, 0.50 mmol) in 2 mL of benzene as described above to give compound **12a** (98 mg, 72%, $R_f = 0.4$ in diethyl ether/ethyl acetate (1:1), colorless oil).

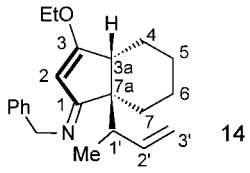


12a

12a. ^{1}H NMR (C_6D_6): δ 6.19 (1 H, m, 2″-H), 5.85 (1 H, m, 2′-H), 5.41 and 5.15 (1 H each, m each, 3″-H$_2$, ^3J = 17.4 and 10.3 Hz), 5.38 (1 H, s, 2-H), 5.04 and 4.99 (1 H each, m each, 3′-H$_2$, ^3J = 15.4 and 9.7 Hz), 4.19 (2 H, m, NCH$_2$), 3.43 (2 H, m, diastereotopic OCH$_2$), 2.78 (1 H, m, 3a-H), 2.56 and 2.35 (1 H each, m each, diastereotopic 1′-H$_2$, J = 8.2 and 13.5), 2.25, 1.95, 1.60, 1.33, and 1.19 (1:1:6:1:1 H, m each, 4-, 5-, 6-, 7-, and 8-H$_2$), 0.99 (3 H, t, 3-OCH$_2$CH_3). ^{13}C NMR (C_6D_6): δ 180.6 and 179.4 (C_q each, C1 and C3), 137.9 (CH, C2″), 135.5 (CH, C2′), 117.5 (CH$_2$, C3′), 114.4 (CH$_2$, C3″), 95.9 (CH, C2), 66.2 (OCH$_2$), 55.0 (NCH$_2$), 52.5 (C_q, C8a), 50.6 (CH, C3a), 47.1 (CH$_2$, C1′), 37.3, 31.7, 28.1, 26.6, and 25.5 (CH$_2$ each, C4−C8), 14.1 (OCH$_2$CH_3). IR (diethyl ether), cm^{-1} (%): 1609.1 (40) [ν(C=N)]. MS (70 eV), *m*/*e* (%): 273 (60) [M$^+$], 244 (100) [M$^+$ − Et], 230 (90) [244 − 14]. HSMS Calcd for $C_{18}H_{27}NO + H^+$: 274.2171. Found: 274.2152.

(3a*R,8a*R**)-(8a-Allyl-3-ethoxy-4,5,6,7,8,8a-hexahydro-3a*H*-azulen-1-ylidene)propylamine (12b).** *N*-Allylpropylamine (**2b**) (50 mg, 0.50 mmol) was reacted with pentacarbonyl[3-(cyclohept-1-enyl)-1-ethoxyprop-2-yn-1-ylidene]tungsten (**1c**) (250 mg, 0.50 mmol) and pyridine (40 mg, 0.50 mmol) in 2 mL of benzene as described above to give compound **12b** by fast chromatography on silica gel (93 mg, 68%, $R_f = 0.4$ diethyl ether/ethyl acetate (1:1), colorless oil). ^{1}H NMR (C_6D_6): δ 5.88 (1 H, m, 2′-H), 5.42 (1 H, s, 2-H), 5.05 and 5.02 (1 H each, m each, 3′-H$_2$, ^3J = 18.5 and 10.1), 3.41 (2 H, t, NCH$_2$), 3.46 (2 H, m, diastereotopic OCH$_2$), 2.80 (1 H, m, 3a-H), 2.60 and 2.38 (1 H each, m each, diastereotopic 1′-H$_2$, J = 8.3 and 13.5 Hz), 2.28, 2.20, 2.00, 1.64, 1.38, and 1.20 (1:1:1:3:3:1 H, m each, 4-, 5-, 6-, 7-, and 8-H$_2$), 1.84 (2 H, m, 2″-H$_2$), 1.09 (3 H, t, 3″-H$_3$), 0.99 (3 H, t, 3-OCH$_2$CH_3). ^{13}C NMR (C_6D_6): δ 179.2 and 179.0 (C_q each, C1 and C3), 135.8 (CH, C2′), 114.2 (CH$_2$, C3′), 95.6 (CH, C2), 65.9 (OCH$_2$), 54.9 (NCH$_2$), 52.2 (C_q, C8a), 50.5 (CH, C3a), 47.3 (CH$_2$, C1′), 37.4, 31.8, 28.2, 26.6, and 21.4 (CH$_2$ each, C4−C8), 25.6 (CH$_2$, C2″), 14.2 (OCH$_2$CH_3), 12.6 (CH$_3$, C3″). IR (diethyl ether), cm^{-1} (%): 1605.0 (40) [ν(C=N)]. MS (70 eV), *m*/*e* (%): 275 (20) [M$^+$], 246 (90) [M$^+$ − C_2H_5], 208 (80) [M$^+$ − C_3H_7N], 206 (90) [M$^+$ − C_5H_9].

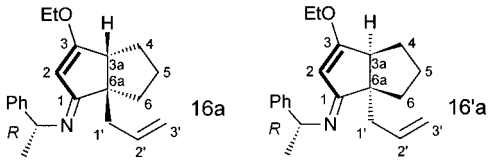
(3a*R,7a*R**)-[7a-(But-1-en-3-yl)-3-ethoxy-4,5,6,7,7a-pentahydro-3a*H*-inden-1-ylidene]benzylamine (14).** *N*-Benzyl(2-butenyl)amine (**13**) (80 mg, 0.50 mmol) was reacted with pentacarbonyl[3-(cyclohex-1-enyl)-1-ethoxyprop-2-yn-1-ylidene]-tungsten (**1b**) (243 mg, 0.50 mmol) and pyridine (40 mg, 0.50 mmol) in 2 mL of benzene as described above to give compound **14** by fast chromatography (100 mg, 65%, $R_f = 0.5$ in diethyl ether/ethyl acetate (1:1), colorless oil).



14

14. ^{1}H NMR (C_6D_6, 600 MHz): δ 7.63, 7.28, and 7.14 (2:2:1, m each, *o*-, *m*-, and *p*-H of C_6H_5), 6.18 (1 H, m, 2′-H), 5.48 (1 H, s, 2-H), 5.02 and 4.98 (1 H each, m each, 3′-H$_2$), 4.72 (2 H, s, NCH$_2$), 3.46 (2 H, br, diastereotopic OCH$_2$), 2.72 (1 H, m, 1′-H), 2.64 (1 H, m, 3a-H), 2.09, 1.76, 1.68, 1.50, 1.45, and 1.32 (1:1:1:1:2:2 H, m each, 4-, 5-, 6-, and 7-H$_2$), 1.05 (3 H, d, 4′-H), 0.98 (3 H, t, 3-OCH$_2$CH_3). ^{13}C NMR (C_6D_6): δ 180.9 and 179.0 (C_q each, C1 and C3), 140.7 (C_q, *ipso*-C of C_6H_5), 140.4 (CH, C2′), 127.5, 127.1, and 125.6 (CH each, 2:2:1, *o*-, *m*-, and *p*-C of C_6H_5), 113.4 (CH$_2$, C3′), 94.9 (CH, C2), 65.4 (OCH$_2$), 55.2 (NCH$_2$), 50.0 (C_q, C7a), 44.6 (CH, C1′), 43.1 (CH, C3a), 27.7, 21.4, 17.1, and 16.7 (CH$_2$ each, C4−C7), 13.5 (CH$_3$, C4′), 13.1 (OCH$_2$CH_3). IR (diethyl ether), cm^{-1} (%): 1604.1 (40) [ν(C=N)]. MS (70 eV), *m*/*e* (%): 323 (15) [M$^+$], 294 (10) [M$^+$ − Et], 232 (10) [M$^+$ − PhCH$_2$], 91 (100) [PhCH$_2^+$].

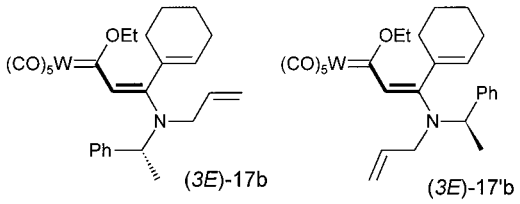
(3a*R*,6a*R*)- and (3a*S*,6a*S*)-[6a-Allyl-3-ethoxy-4,5,6,6a-tetrahydro-3a*H*-pentalen-1-ylidene](1-phenylethyl)-amine (16a and 16′a). *N*-Allyl[(*R*)-(1-phenylethyl)]amine (**15**) (80 mg, 0.50 mmol) was reacted with pentacarbonyl[3-(cyclopent-1-enyl)-1-ethoxyprop-2-yn-1-ylidene]tungsten (**1a**) (236 mg, 0.50 mmol) and pyridine (40 mg, 0.50 mmol) in 2 mL of benzene as described above to give a 2:3 mixture of compounds **16a** and **16′a** (91 mg, 59%, $R_f = 0.5$ in diethyl ether/ethyl acetate (1:1), colorless oil).



16a [16′a]. ^{1}H NMR (C_6D_6): δ 7.61, 7.27, and 7.12 [7.61, 7.27, and 7.12] (2:2:1, m each, *o*-, *m*-, and *p*-H of C_6H_5), 5.97 [5.76] (1 H, m, 2′-H), 5.35 [5.36] (1 H, s, 2-H), 5.04 [4.93] (2 H, m, 3′-H$_2$), 4.65 [4.65] (1 H, m, NCH), 3.36 [3.37] (2 H, m, diastereotopic OCH$_2$), 2.78 and 2.32 [2.79 and 2.32] (1 H each, m, 1′-H$_2$), 2.80 [2.80] (1 H, m, 3a-H), 2.27 and 1.73 [2.27 and 1.73], 1.47 [1.47], and 1.15 [1.15] (1:1:2:2 H, m each, 4-H$_2$−6-H$_2$), 1.60 [1.62]) [3 H, d, NCH(Ph)CH_3], 0.96 [0.97]) (3 H, t, 3-OCH$_2$CH_3). ^{13}C NMR (C_6D_6): δ 178.9 and 177.7 [179.9 and 177.7] (C_q each, C1 and C3), 148.2 [148.2] (C_q, *ipso*-C of C_6H_5), 136.3 [136.7] (CH, C2′), 128.5, 127.1, and 126.4 [128.5, 127.1, and 126.4] (CH each, 2:2:1, *o*-, *m*-, and *p*-C of C_6H_5), 116.9 [116.9] (CH$_2$, C3′), 95.4 [95.6] (CH, C2), 66.1 [66.1] (OCH$_2$), 61.1 [61.0] (NCH), 57.4 [57.3] (C_q, C6a), 50.5 [50.5] (CH, C3a), 43.4 [43.2] (CH$_2$, C1′), 38.5, 29.5, and 26.0 [38.6, 29.6, and 25.9] (CH$_2$ each, C4−C6), 24.8 [24.8] [CH$_3$, NCH(Ph)CH_3], 14.1 [14.1] (OCH$_2$CH_3). IR (diethyl ether), cm^{-1} (%): 1606.2 (40) [ν(C=N]. MS (70 eV), *m*/*e* (%): 309 (40) [M$^+$], 280 (20) [M$^+$ − Et], 105 [PhCHCH$_3$] (100). HSMS Calcd for $C_{21}H_{27}NO + H^+$: 310.2171. Found: 310.2155.

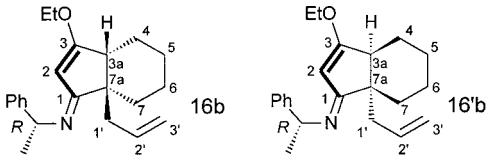
1,1,1,1,1-Pentacarbonyl-4-(cyclohex-1-enyl)-2-ethoxy-4-[(1-phenylethyl)allylamino]-1-tungsta-1,3-butadiene [(3*E*)-17b and (3*E*)-17′b] and (3a*R,7a*R**)- and (3a*S**,6a*S**)-[6a-Allyl-3-ethoxy-4,5,6,7,7a-pentahydro-3a*H*-inden-1-ylidene](1-phenylethyl)amine (16b and 16′b).** *N*-Allyl[(*R*)-(2-phenylethyl)]amine (**15**) (80 mg, 0.50 mmol) was reacted with pentacarbonyl[3-(cyclohex-1-enyl)-1-ethoxyprop-2-yn-1-ylidene]tungsten (**1b**) (243 mg, 0.50 mmol) in *n*-pentane/diethyl ether (3:1) at −20 °C as described above to give a 10:9 mixture of rapidly interconverting compounds **17b**/**17′b** (286 mg, 85%,

$R_f = 0.7$ in *n*-pentane/dichloromethane (2:1), yellow crystals, mp 79 °C).[18] Compound **17b**/**17′b** (161 mg, 0.25 mmol) and pyridine (20 mg, 0.25 mmol) in 2 mL of benzene were heated to 60 °C for 2 h. Workup as described above gave a 2:3 mixture of polar compounds **16b**/**16′b** (50 mg, 63%, $R_f = 0.5$ in diethyl ether/ethyl acetate (1:1), colorless oil).



17b [17′b]. ^{1}H NMR ($CDCl_3$, −20 °C): δ 7.49, 7.35, and 7.24 [7.40, 7.35, and 7.24] (2:2:1, m each, *o*-, *m*-, and *p*-H of C_6H_5), 6.55 [6.53] (1 H, s, 3-H), 5.70 [5.77] (1 H, m, 2′-H), 5.34 [5.34] [1 H, m, CH of N(allyl)], 5.32 [5.45] (1 H, m, NC*H*), 5.21 [5.17] [2 H, m, CH_2 of N(allyl)], 4.61 [4.61] (2 H, m, 3-OCH_2), 3.82 and 3.63 [3.82 and 3.63] [1 H each, m each, NCH_2 of N(allyl)], 2.34 and 2.06 [2.34 and 2.06], 2.15 [2.15], 1.79 and 1.53 [1.79 and 1.53], 1.76 [1.76], (1:2:2:1 H, m each, 3′-H_2−6′-H_2), 1.58 [1.64] [3 H, d, NCH(Ph)CH_3], 1.43 [1.27] (3 H, t, 3-OCH_2CH_3). ^{13}C NMR ($CDCl_3$): δ 269.5 (270.4) (C_q, C2), 204.5 and 199.5 [204.5 and 199.5] [C_q each, *trans*- and *cis*-CO of $W(CO)_5$], 158.5 [158.1] (C_q, C4), 134.5 [134.7] (C_q, C1′), 131.7 [131.9] [CH of N(allyl)], 125.7 [126.1] (CH, C2′), 120.1 [120.2] (CH, C3), 118.4 [118.4] [CH_2 of N(allyl)], 77.2 [77.0] (OCH_2), 57.4 [56.2] (NCH), 48.9 [48.5] (NCH_2), 27.8, 24.6, 21.9, and 21.1 [27.8, 24.6, 21.9, and 21.2] (CH_2 each, C3′−C5′), 18.1 [17.8] [NCH(Ph)CH_3], 16.1 [16.0] (OCH_2CH_3). IR (diethyl ether), cm^{-1} (%): 2053.1 (5), 1912.2 (100), and 1893.6 (70) [ν(C═N)]. MS (70 eV), *m*/*e* (^{184}W) (%): 674 (5) [M^+], 534 (40) [M^+ − 5 CO]. Anal. Calcd for $C_{27}H_{29}NO_6W$ (647.4): C, 50.09; H, 4.52; N, 2.16. Found: C, 49.83; H, 4.55; N, 1.89.

(18) For a more detailed NMR study of this dynamic process see ref 8.



16b [16′b]. ^{1}H NMR (C_6D_6): δ 7.66, 7.27, and 7.12 [7.66, 7.27, and 7.12] (2:2:1, m each, *o*-, *m*-, and *p*-H of C_6H_5), 5.78 [5.94] (1 H, m, 2′-H), 5.39 [5.36] (1 H, s, 2-H), 5.10 [4.94] (2 H, m, 3′-H_2), 4.72 [4.72] (1 H, m, NCH), 3.44 [3.35] (2 H, m, diastereotopic OCH_2), 2.77 and 2.32 [2.77 and 2.33] (1 H each, m, 1′-H_2), 2.67 [2.67] (1 H, m, 3a-H), 2.04 and 1.55 [2.04 and 1.55], 1.72 [1.72], 1.48 [1.48], and 1.33 [1.33] (1:1:2:2:2 H each, m each, 4-H_2−7-H_2), 1.66 [1.67] [3 H, d, NCH(Ph)CH_3], 0.95 [0.94] (3 H, t, 3-OCH_2CH_3). ^{13}C NMR (C_6D_6): δ 180.8 and 177.4 [180.8 and 177.4] (C_q each, C1 and C3), 147.6 [147.7] (C_q, *ipso*-C of C_6H_5), 135.5 [135.7] (CH, C2′), 128.6, 127.0, and 126.5 [128.6, 127.1, and 126.6] (CH each, 2:2:1, *o*-, *m*-, and *p*-C C_6H_5), 117.3 [117.3] (CH_2, C3′), 94.5 [94.4] (CH, C2), 66.3 [66.3] (OCH_2), 60.8 [60.6] (NCH), 48.2 [48.1] (C_q, C7a), 45.1 [45.0] (CH, C3a), 43.8 [43.6] (CH_2, C1′), 31.5, 25.6, 19.1, and 19.0 [31.7, 25.6, 19.0, and 18.9] (CH_2 each, C4−C7), 22.5 [22.5] [CH_3, NCH(Ph)CH_3], 14.1 [14.1] (OCH_2CH_3). IR (diethyl ether), cm^{-1} (%): 1604.3 (30) [ν(C═N)]. MS (70 eV), *m*/*e* (%): 323 (40) [M^+], 281 (45) [$M^+ - 42$], 105 [$PhCHCH_3^+$] (100). HSMS Calcd for $C_{22}H_{29}NO + H^+$: 324.2327. Found: 324.3235.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

Supporting Information Available: Details of the X-ray crystal structure analyses of compounds **6a** and **10c**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM010045O